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## Time-Resolved Morphology Development of Tri-axial Reinforced Epoxy Montmorillonite Nanocomposites in Uni-Axial Magnetic Fields

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*Numerous papers and patents have been published on polymeric nanocomposites. However, extensive research has not yielded nanocomposites with vastly improved properties, as was envisioned, but has instead mimicked the results of conventionally filled systems. This is mostly due to a poor nanoparticle-matrix interface and the lack of control over dispersion and orientation of nanofillers to an extent comparable to what has been accomplished in continuous fiber reinforced composites. Utilizing the orthogonal magnetic susceptibility of Montmorillonite nanocomposites (MMTs) from different deposits with comparable Fe content (3.4%), we have generated a three-dimensional morphology composed of orthogonally aligned aluminosilicate layers from a mixture of Montmorillonites subjected to a uniaxial external magnetic field. Depending on the source, MMTs exhibit remnant magnetization arising from antiferro- and ferromagnetic impurities, and align with their layers parallel or perpendicular to the field. In-situ X-ray measurements show that within a few minutes an applied static magnetic field (1.2 or 11.7 Tesla) induces the stable alignment of an organically-modified MMT within an epoxy resin at room temperature. Structural relaxation is orders of magnitude slower. Overall, these studies demonstrate that a critical component of the chemistry in these nanofillers has been overlooked in the past. Remarkably minor compositional differences may allow researchers to explore many more possible techniques to address nanocomposite issues.*

Real-time x-ray experiments were carried out at beamline X27C at the NSLS using a marCCD detector at a sample-to-detector distance of 82.5 cm. Two types of layered silicates, Southern Clay MMT modified with octadecylamine (SC18) and Nanocor I30.E (NC18), were dispersed in epoxy (an Epon 862 monomer) via sonication and high-shear mixing. After additional short mixing with a curing agent and subsequent degassing, the suspensions were deposited into x-ray capillaries for use in a 1.2-Tesla rare-earth permanent magnet.

The morphology response to the application of the magnetic field at room temperature ( $\sim 27^\circ\text{C}$ ) was monitored in-situ by positioning the magnet such that the x-ray beam passed between the poles of the magnet and through the capillary. The capillaries were dropped into the magnetic field remotely via a solenoid switch and a paper clip attached to the top of the capillary. After alignment, the capillary was removed from the magnet and repositioned within the beam to examine the degree of randomization, or was fixed by a two-stage curing reaction (120  $^\circ\text{C}$  for 2 hours; 175  $^\circ\text{C}$  for two hours).

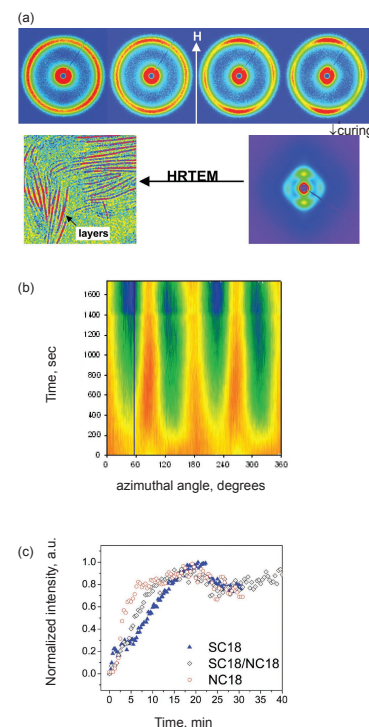
**Figure 1** reveals that alignment of the 3 wt% SC18/NC18 mixture is 90% complete after 10 minutes in the 1.2-Tesla magnetic field at room temperature. **Figure 1a** shows a series of x-ray patterns at three-minute time intervals during the alignment process of that mixture. The final pattern was taken after a complete cure cycle and shows the partial exfoliation of the system, with the d-spacings of the galleries increasing from 3.7 nm to 12.5 nm. For this mixture, a two-dimensional contour plot of azimuthal scans at the  $d_{001}$  reflections

is shown in **Figure 1b**. This plot emphasizes the rapid formation of the four-point pattern, which reflects triaxial reinforcement by the OMM layers. A plot of the intensity of the  $d_{001}$ -layer diffraction at an azimuthal angle of 0 degrees (meridian) (**Figure 1c**) shows that steady-state alignment of the SC18/NC18 mixture (3wt% total) within the 1.2-Tesla magnetic is achieved after 15 minutes. This time scale is very similar to other OMMs and no indication of faster or slower orientation has been observed.

These experiments also show that once alignment has been achieved the sample does not quickly relax back to its random alignment, which is in agreement with rheology studies on similar systems. Alignment is possible in several solvents (Toluene, water) and epoxy monomers (Epon 862, Epon 828). The slow relaxation behavior is to be expected, considering the matrix viscosity and the Brownian motion of particles at room temperature. Rotational diffusion is hindered by particle-particle interaction and the high viscosity of the epoxy resin formulation.

The magnetic field alignment does not affect the curing chemistry, which agrees with electric field experiments on the same system.

Measurements on the coefficient of thermal expansion (CTE) confirm that morphology control leads to significant differences depending on the alignment of the layered silicates, decreasing CTE the most in the direction of maximum MMT alignment. Understanding the detailed mechanism that leads to a change of the magnetic easy axis within layered silicates opens up opportunities to design novel synthetic layered silicates with unusual magnetic properties.



**Figure 1.** a) A series of x-ray patterns of a 3 wt% SC18/NC18 suspension in Epon 862 at room temperature. Orthogonal alignment of the two different clays starts at about five minutes. Beginning to end (left to right) is 30 minutes. The last image shows the fully cured nanocomposite with a false color HRTEM to the left; b) 2D contour plot with azimuthally averaged line scans through the gallery diffraction peak at 3.7 nm showing the four point pattern development with time; c) normalized intensity at 90 degrees of azimuthal scan versus time for 3 wt% SC18, NC18 and SC18/NC18 in Epon 862.